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(54) **Beverage antioxidant system**

(57) An antioxidant system for ready-to-drink beverages and beverage concentrates. The antioxidant system is particularly suitable for coffee beverages. The

antioxidant system is made up of glucose oxidase, a glucose oxidase substrate, a catalase and an inorganic oxygen scavenger. The beverages have improved aroma and flavour.

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## Description

[0001] This invention relates to an antioxidant system for beverages; especially beverages in ready-to-drink form. The invention also relates to beverages and beverage precursors which contain the antioxidant system and to processes for removing oxygen using the antioxidant system.

[0002] Many beverages suffer adverse effects from exposure to oxygen. This is particularly the case with ready-to-drink beverages; especially ready-to-drink coffee beverages. Ready-to-drink coffee beverages are produced by extracting soluble coffee solids from roasted and ground coffee beans using hot water. The extract obtained may then be diluted to a desired concentration, usually to contain about 1% by weight of soluble coffee solids. Various additives are added to the diluted extract which is then filled into containers. The containers are then sealed and subjected to retorting. Certain intermediate steps may also be carried out. For example, the extract may be concentrated and dried to powder prior to formation of the dilute extract. This is usually done when the coffee is filled into the containers at a site different than the site at which the extraction is carried out.

[0003] During this process, the coffee may be exposed to oxygen several times. For example, oxygen may be present in the hot water which is used to extract the soluble coffee solids from the roasted and ground coffee beans. Also, the coffee may be exposed to oxygen during extraction or subsequent processing such as concentration and drying. Further, oxygen may get into the container during filling. No matter where in the process the coffee is exposed to oxygen, it is now recognised that the oxygen adversely effects the flavour and aroma of the coffee beverage. In particular, the beverage loses its fresh, clean flavour and aroma; the flavour and aroma which characterises freshly brewed coffee. Often, bitter, acid flavours develop.

[0004] Various measures have been taken in the past to reduce the influence of oxygen. Usually these methods have centred on preventing ingress of oxygen. For example, Japanese patent application 6-141776 discloses extracting coffee grounds using deoxygenated water in an inert gas atmosphere. Further, all subsequent steps, including filling of the dilute extract into containers, is done under inert gas atmosphere. The patent application describes the resulting product to have a good, fresh flavour. The inert gas recommended is nitrogen. The primary problem with this technique is its cost. Carrying out an entire extraction and filling process in a nitrogen gas atmosphere is extremely expensive. Also, deoxygenating water is not a perfect process and not all oxygen is removed.

[0005] Another approach which has been attempted is to use antioxidants during the process. For example, US patent 5,384,143 describes a process in which the coffee extract is rapidly cooled to below 20°C and then an antioxidant selected from erythorbic acid, ascorbic acid, and their water soluble salts, is added to the cooled extract. The extract is then filled into cans under oxygen free conditions. This technique is less expensive than carrying out the entire process under inert gas atmosphere but there are problems. In particular, coffee is a potent antioxidant which is able to scavenge oxygen faster than most antioxidants commonly used in foods. Therefore, although the antioxidants described in this patent remove some of the oxygen, they are not potent enough to prevent the coffee from scavenging a large portion of the oxygen present. Consequently, the coffee undergoes some oxidative damage.

[0006] A further approach has been the use of enzyme systems. For example, the use of systems based upon glucose oxidase and alcohol oxidase have been suggested. However these systems have not proved to be adequate since degradation due to oxygen still occurs. Also, these enzyme systems often produce hydrogen peroxide which is undesirable.

[0007] Therefore it is an object of this invention to provide an antioxidant system which is relatively inexpensive and which is sufficiently potent to remove oxygen from beverage components which are themselves antioxidants.

[0008] Accordingly, in one aspect, this invention provides an antioxidant system for ready-to-drink beverages, the system comprising glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger.

[0009] It has been surprisingly found that the combination glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger is a sufficiently potent antioxidant such that small amounts are able to adequately compete with beverage components which are potent antioxidants, such as coffee. Since small amounts are required, the system therefore offers the advantage of being an inexpensive and effective antioxidant. Also, the system is food grade; especially at the small amounts required.

[0010] In another aspect, this invention provides a ready-to-drink beverage which includes an antioxidant system, the system comprising glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger.

[0011] The ready-to-drink beverage is preferably a coffee beverage; especially a black coffee beverage. The ready-to-drink beverage may be retorted.

[0012] In a yet further aspect, this invention provides a beverage concentrate which includes an antioxidant system, the system comprising glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger.

[0013] The inorganic oxygen scavenger is preferably a sulphite; for example sodium sulphite.

[0014] In another aspect, this invention provides a process for reducing oxygen in a beverage, the process comprising:

adding an antioxidant system comprising glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger to the beverage;  
 filling the beverage into containers; and  
 sealing the containers.

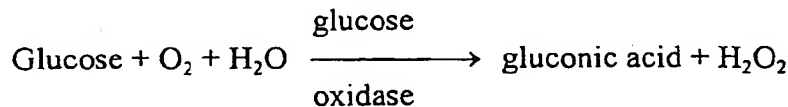
[0015] In another aspect, this invention provides a process for reducing oxygen in a beverage containing extracted solids, the process comprising:

adding an antioxidant system comprising glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger to an extraction liquid;  
 extracting solids from an extraction substrate using the extraction liquid to provide a beverage;  
 filling the beverage into containers; and  
 sealing the containers.

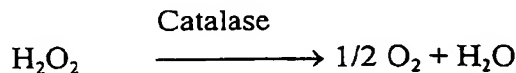
[0016] Preferably, the beverage is filled into containers under oxygen reduced or oxygen free conditions. Further, further amounts of the antioxidant system may be added to the beverage prior to sealing of the containers.

[0017] Embodiments of the invention are now described, by way of example only. This invention provides an antioxidant system which is useful for removing oxygen from beverages and beverage concentrates. The antioxidant system may be used, for example, during the processing of the beverage, in a pre-cursor to the beverage such as a beverage concentrate, or in ready-to-drink beverages. The antioxidant system is particularly suitable for use in connection with ready-to-drink, coffee beverages and will be described primarily in this context. It is to be appreciated however that this is done for simplicity of description and the antioxidant system is not limited to this application.

[0018] The antioxidant system includes a glucose oxidase (EC 1.1.3.4). The glucose oxidase catalyses the oxidation of glucose to gluconic acid according to the following reaction scheme:



[0019] The antioxidant system also includes a catalase (EC 1.11.1.6). Then, the catalase degrades the peroxide according to the following reaction scheme:



[0020] The glucose oxidase and the catalase are preferably provided in the form of an enzyme mixture. A suitable enzyme mixture is the Novozym® 358 enzyme preparation commercialised by Novo Nordisk AS of Novo Allé, 2880 Bagsvaerd, Denmark. This enzyme preparation is prepared from *Aspergillus niger* and is generally recognised as safe.

[0021] The antioxidant system also includes a glucose oxidase substrate. This takes the form of glucose. The glucose oxidase substrate may be an inherent part of the beverage itself, may be added to the beverage, or both. In the case of coffee beverages, the glucose oxidase substrate is ordinarily added to the beverage mix because coffee contains little or no glucose. However, for other beverages which inherently contain glucose, further glucose need not be added.

[0022] The antioxidant system further includes an inorganic oxygen scavenger. Sulphites are particularly useful as inorganic oxygen scavengers. Suitable sulphites include sulphur dioxide, sodium sulphite, sodium metabisulphite, anhydrous sodium bisulphite, potassium metabisulphite, anhydrous potassium bisulphite, and mixtures of these agents. Sodium sulphite is particularly preferred. Apart from further removing oxygen, the inorganic oxygen scavenger removes hydrogen peroxide generated by the glucose oxidase.

[0023] The amount of the antioxidant system used will depend upon the substance to be treated and the level of oxygen present. Also, the amounts used of the various components in the antioxidant system will depend upon the substance to be treated and the level of oxygen present. Further, the amount of enzyme used will depend upon the activity of the enzyme. These amounts will be readily determined for each situation.

[0024] However, in general, the amount of glucose oxidase used is less than about 0.5% by weight of the total weight of the substance to be treated. For example, the amount of glucose oxidase used is preferably in the range of about 0.001% to about 0.1% by weight of the total weight of the substance to be treated. An amount in the range of about

0.005% to about 0.05% by weight is especially preferred for coffee beverages. The activity of the glucose oxidase is preferably about 1500 units/ml to about 2500 units/ml; for example about 2000 units/ml. A unit is the amount of enzyme which, at a temperature of 25°C and a pH of 5.1, catalyses the formation of 1  $\mu$ mol of  $H_2O_2$ .

[0025] The amount of glucose oxidase substrate which is used is conveniently less than about 1% by weight of the total weight of the substance to be treated. For example, the amount of glucose oxidase substrate used is preferably in the range of about 0.005% to about 0.5% by weight of the total weight of the substance to be treated. An amount in the range of about 0.01% to about 0.3% by weight is especially preferred for coffee beverages; for example about 0.05% by weight. The glucose oxidase substrate may be present in the substance to be treated or may be added to the substance, or both. Usually, for coffee beverages, the glucose oxidase substrate is added. For beverages which must undergo heat treatment, the amount of glucose oxidase substrate used is preferably kept to the minimum necessary to obtain the required glucose oxidase activity. In this way, the formation of undesirable Maillard reactions may be avoided.

[0026] The amount of the inorganic oxygen scavenger which is used is conveniently less than about 0.1% by weight of the total weight of the substance to be treated. For example, the amount of inorganic oxygen scavenger used is preferably in the range of about 0.001% to about 0.05% by weight of the total weight of the substance to be treated. An amount in the range of about 0.002% to about 0.03% by weight is especially preferred for coffee beverages; for example about 0.005% by weight. Further, relevant regulatory requirements concerning the maximum residual levels of inorganic oxygen scavengers in foodstuffs should be respected.

[0027] If a catalase is used, the amount used is not critical. Usually the catalase will be provided in a mixture with the glucose oxidase and hence the catalase levels will be determined by the amount of glucose oxidase used.

[0028] The antioxidant system may be used at various points during the processing of a beverage. For example, for coffee and tea beverages, the antioxidant system may be added to the water which is to be used to extract soluble solids from the coffee or tea. In this way, the water which is used for extraction may be efficiently deoxygenated. However, because the glucose oxidase denatures at temperatures above about 60°C, the treatment should be carried out prior to heating the extraction water.

[0029] The antioxidant system may also be added to the extract obtained after extraction. At the time of addition of the enzyme of the antioxidant system, the temperature of the extract should be below about 60°C. After the extract has been deoxygenated, the extract may be thermally treated; for example during concentration or drying or both. The inorganic oxygen scavenger continues to operate at temperatures above 60°C. Of course, for best effect, all further processing of the extract should be carried out under oxygen reduced or oxygen free conditions. The various techniques described in the art may be used. In this way, a beverage, beverage concentrate or beverage powder which contains the antioxidant system and low levels of oxygen may be obtained.

[0030] The antioxidant system may also be added to the beverage prior to filling of the beverage into containers. At the time of addition of the enzyme of the antioxidant system, the temperature of the beverage should be below about 60°C. After the beverage has been deoxygenated, the beverage may be retorted in the usual manner. For best effect, the subsequent filling of the beverage into containers may be carried out under oxygen reduced or oxygen free conditions. The various techniques described in the art may be used. The beverage obtained preferably contains less than about 1 ppm of dissolved oxygen; more preferably less than about 0.5 ppm dissolved oxygen.

[0031] The antioxidant system may be used in combination with any type of beverage such as tea beverages, coffee beverages, chocolate beverages, malted beverages, and the like. However the system is particularly suited for use in coffee beverages since the system is able to compete with the potent antioxidant effects of coffee. Black coffee beverages, which are intended to have a clean, fresh flavour and aroma, are especially suitable. These beverages ordinarily contain about 0.5% to about 1.5% by weight of soluble coffee solids. They may also contain a sweetener.

[0032] Specific examples are now described to further illustrate the invention.

#### Example 1

[0033] Three beverages are prepared and are standardised to contain about 8 ppm of dissolved oxygen. The first beverage (beverage 1) is freshly brewed coffee which contains 1% by weight of soluble coffee solids. The second beverage (beverage 2) is prepared from a commercially available instant coffee and contains 1% by weight of soluble coffee solids. The third beverage (beverage 3) is freshly brewed coffee which contains 1% by weight of soluble coffee solids, 0.1% by weight of Novozym® 358 enzyme preparation, 0.1% by weight of glucose, and 0.008% by weight of sodium sulphite. The beverages are held in containers open to the ingress of air and the concentration of dissolved oxygen is determined at regular intervals.

[0034] The results are as follows:

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Time (minut s)	Dissolved O <sub>2</sub> (ppm) Beverag 1	Dissolv d O <sub>2</sub> (ppm) Beverage 2	Dissolved O <sub>2</sub> (ppm) B verage 3
0	8	8	8
5	4.7	7.5	2
10	4.3	7.0	0.4
15	4.1	6.6	0.5
20	3.9	6.4	0.5
25	3.6	6.1	0.5
30	3.4	6.0	0.5
35	3.3	6.0	0.5
40	3.2	5.9	0.5
45	3.1	5.9	0.5
50	3.0	5.9	0.5
55	3.0	5.9	0.5
60	3.0	5.9	0.5

[0035] The results indicate the antioxidant system in beverage 3 removes dissolved oxygen much faster than freshly brewed and instant coffee. Therefore the antioxidant system is able to adequately compete with the coffee for oxygen; hence protecting the coffee from oxygen damage.

## Example 2

[0036] Cans containing coffee solids are prepared. All cans contain about 1% by weight of coffee solids, about 5% by weight of sugar, about 0.065% by weight of sodium bicarbonate, and about 0.01% by weight of lysine. All cans are filled and sealed under the same conditions. During filling, the contents of each can are exposed to air.

[0037] Certain of the cans (the "Test cans") also contain an antioxidant system of 0.1% by weight of glucose, 0.01% by weight of Novozym® 358 enzyme preparation, and 0.005% by weight of sodium sulphite. The other cans form a control (the "Control cans").

[0038] After 1 hour, 1 can from each group is opened and the dissolved oxygen is determined. The remaining cans of each group are then retorted and allowed to cool. After 12 days, a can of each group is opened and a sensory panel is used to analyse the aroma and flavour of the sample.

Group	Time (hours)	Dissolved O <sub>2</sub> (ppm)	Aroma & Flavour
Test	1	0.9	Fresh, clean flavours and aroma with roasty notes. Less acidity.
Control	1	6.8	Acid notes present. Prune-like, bland flavour.

[0039] The beverage of the test group has much less dissolved oxygen and much improved flavour and aroma.

[0040] Unopened cans of each group are stored for 10 weeks at room temperature and are then opened. The pH is determined. The beverage of the Control cans has a pH of about 5.5 while the beverage of the Test cans has a pH of about 5.7. A sensory panel is used to analyse the aroma and flavour of the beverage of the Test cans and it is found to have fresh, clean flavours and aroma.

## Example 3

[0041] Roast and ground coffee is placed in an extraction system. The conditions are not oxygen free. The coffee is then xtracted with one of three diff rent typ s of deionised water at a temperature of about 25°C to 40°C. The first type, Type A, is untr ated d ionised water. Th s cond typ , Typ 1, is deionised water which is tr ated with an antioxidant system of 0.05% by w ight of glucose, 0.01% by weight of Novozym® 358 enzyme preparation, and 0.005% by weight of sodium sulphite. The third type, Type 2, is deionised water which is treated with an antioxidant system of

0.05% by weight of glucose, 0.1% by weight of Novozym® 358 enzyme preparation, and 0.005% by weight of sodium sulphite. The dissolved oxygen content of each type of deionised water and each extract is determined.

[0042] Each extract obtained is diluted with a sugar solution to provide a coffee beverage containing about 1% by weight of coffee solids. Each beverage is then filled into cans and the cans sealed. A can of each beverage is opened and the dissolved oxygen content of the beverage is determined. The remaining cans are retorted.

Water Type	O <sub>2</sub> Conc (ppm) in Extraction Water	O <sub>2</sub> Conc (ppm) in Extract	O <sub>2</sub> Conc (ppm) in Beverage
A	7.79	2.54	0.81
1	2.96	0.86	0.08
2	0.04	0.15	0.07

[0043] The results indicate that reducing the oxygen content of the extraction liquid greatly reduces the oxygen content in the resultant beverage, despite the beverage being produced under conditions which are not oxygen free.

[0044] Unopened cans of each group are stored for 10 weeks at room temperature and are then opened. A sensory panel is used to analyse the aroma and flavour of the beverages in the cans. The beverages produced using water Types 1 and 2 have a fresh, clean flavour and aroma. The beverages produced using water Type A have an unacceptable flavour and aroma.

## Claims

1. A ready-to-drink beverage which includes an antioxidant system, the system comprising an enzyme composition containing a glucose oxidase, a glucose oxidase substrate and a catalase, and an inorganic oxygen scavenger.
2. A beverage according to claim 1 which contains about 0.001% to about 0.1% by weight of glucose oxidase.
3. A beverage according to claim 1 or claim 2 which contains about 0.005% to about 0.5% by weight of glucose oxidase substrate.
4. A beverage according to any of claims 1 to 3 in which the inorganic oxygen scavenger is a sulphite.
5. A beverage according to claim 4 which contains about 0.001% to about 0.05% by weight of sulphite.
6. A beverage according to claim 4 or claim 5 in which the sulphite is sodium sulphite.
7. A beverage according to any of claims 1 to 6 which is a black coffee beverage.
8. A beverage concentrate which includes an antioxidant system, the system comprising an enzyme composition containing a glucose oxidase, a glucose oxidase substrate, and a catalase, and an inorganic oxygen scavenger.
9. A process for reducing oxygen in a beverage, the process comprising:  
adding an antioxidant system comprising glucose oxidase, a glucose oxidase substrate, a catalase and an inorganic oxygen scavenger to the beverage;  
filling the beverage into containers; and  
sealing the containers.
10. A process for reducing oxygen in a beverage containing extracted solids, the process comprising:  
adding an antioxidant system comprising glucose oxidase, a glucose oxidase substrate, a catalase and an inorganic oxygen scavenger to an extraction liquid;  
extracting solids from an extraction substrate using the extraction liquid to provide a beverage;  
filling the beverage into containers; and  
sealing the containers.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 99 20 0185

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Section Ch, Week 7515 Derwent Publications Ltd., London, GB; Class A18, AN 75-24824W XP002104391 & JP 49 082590 A (TANABE SEIYAKU CO) , 8 August 1974 * abstract *	1-10	A23L3/3436 A23L2/44 A23L2/84
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X	DATABASE FSTA INTERNATIONAL FOOD INFORMATION SERVICE (IFIS), FRANKFURT/MAIN, DE AN 77-1-09-t0523, 1977 "Preservative" XP002104428 * abstract * & JP 05 203630 A	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) A23L
X	SCHOBINGER U. ET AL.: "Glucoseoxidase zur Verminderung der Sauerstoffbelastung bei der Abfüllung von Getränken" MITT. KLOSTERNEUBURG, vol. 39, no. 6, 1989, pages 251-256, XP002104389 * page 252, left-hand column * * page 253 * --- -/--	1-10	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 1 June 1999	Examiner Bendl, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1500 (3.92) (P4/001)



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## EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	SCHOBINGER U. ET AL.: "Glucoseoxidase zur Verminderung der Sauerstoffbelastung bei der Abfüllung von Getränken" FLÜSSIGES OBST, vol. 59, no. 10, 1992, pages 586-588, 590, XP002104390 * page 586 *	1-10	
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			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 1 June 1999	Examiner Bendl, E
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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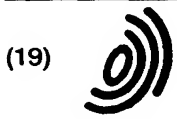
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82





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(54) **Mélange précurseur d'arôme**

(57) Mélange précurseur d'arômes générant, lors d'une étape de chauffage, une note aromatique due à la formation de thiols.

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## Description

[0001] La présente invention a pour objet un mélange précurseur d'arômes et son utilisation lors de la fabrication de compositions alimentaires.

[0002] Il est connu que les composés contenant du soufre sont des constituants importants dans le domaine des arômes alimentaires.

[0003] En effet, il est connu, dans "BACIS, VCF96, database of volatile compounds in food 1996" que les groupes thiols sont présents dans les arômes alimentaires, dégageant une odeur de rôti, une odeur de grillé formées lors de la cuisson de certaines compositions alimentaires, telles que, notamment, les viandes, les oeufs ou les végétaux, lors du procédé de fabrication de la bière ou lors du rôtissage du café, par exemple.

[0004] Malheureusement, les thiols sont des composés instables qui sont souvent perdus par évaporation ou par oxydation. Hofmann et al. dans J. Agric Food Chem., 1996, 44, 251-255, ont montré que les thiols sont oxydés en disulfures correspondants, après un stockage à une température de 6° C.

[0005] Par ailleurs, Mottram et al., dans J. Agric Food Chem., 1996, 44, 2349-2351, soutiennent que les groupements thiols peuvent être formés, en faisant réagir dans une solution aqueuse à chaud, des composés disulfures avec des protéines comprenant des groupes sulphydryles, notamment des cystéines, ou des ponts disulfures, notamment des cystines. Dans ce document, ils mettent notamment en évidence le fait que la cuisson d'une solution aqueuse contenant un disulfure et de l'albumine permet la libération de groupes thiols, à un rendement de 44,8%.

[0006] Le but de la présente invention est de proposer un mélange précurseur d'arômes permettant de favoriser le dégagement d'une odeur de grillé ou d'une odeur de rôti précisément lors de la cuisson ou lors du réchauffage de compositions alimentaires.

[0007] A cet effet, la présente invention a pour objet un mélange précurseur d'arômes générant lors d'une étape de chauffage, une note aromatique due à la formation de thiols.

[0008] La présente invention a permis de mettre en évidence la nécessité de la présence de un ou plusieurs groupements sulphydryles que l'on fait réagir avec un ou plusieurs polysulfures, de manière à permettre le dégagement d'une note aromatique.

[0009] Dans la suite de la description, on emploiera indifféremment l'expression "note aromatique" ou le terme "odeur" pour désigner la formation d'un arôme perceptible, sur le plan sensoriel, au niveau de l'odorat ou par voie retro-nasale.

[0010] De préférence, le mélange précurseur d'arômes est constitué d'un polysulfure et d'une source de soufre non volatile comprenant au moins un groupe sulphydryle.

[0011] De préférence, le polysulfure est de type  $R-(S)_n-R'$  où R et R' sont identiques ou différents et n est supérieur ou égal à 2. On peut notamment utiliser comme polysulfure un diméthyl disulfure, un bis(2-furfuryl)disulfure, un bis(3-méthyl-2-furanyl)disulfure, un bis(3-méthyl-2-butén-1-yl)disulfure ou un disulfure de thio-cétones, comme le bis-(2-oxopropyl) disulfure.

[0012] La présente invention concerne également un système aromatique dans lequel le polysulfure est obtenu par biotransformation d'un conjugué cystéine-aldéhyde à l'aide d'une levure boulangère dans un tampon phosphate à pH 7-9, de préférence à pH 8, contenant 10-30 mM de conjugué cystéine-aldéhyde.

[0013] La source de soufre non volatile, combinée ou non à d'autres constituants, peut être un acide aminé soufré, un peptide contenant au moins un acide aminé soufré, une protéine contenant au moins un acide aminé soufré et/ou un hydrolysate de protéines contenant au moins un acide aminé soufré, par exemple.

On peut utiliser comme source de soufre non volatile, selon la présente invention, de la cystéine, du glutathion, de l'albumine d'oeuf, du gluten, du BSA, des protéines de lait ou des hydrolysats de protéines de lait, par exemple.

[0014] De préférence on chauffe à pH neutre le mélange, selon l'invention, de manière à permettre la formation de thiols à un rendement de 48-90%.

[0015] La présente invention a également pour objet l'utilisation d'un tel mélange précurseur d'arômes dans la fabrication d'une composition alimentaire, de manière à favoriser le développement d'une note aromatique rôtie, grillée lorsqu'on chauffe la composition alimentaire en milieu aqueux ou à sec.

[0016] On peut notamment utiliser un tel mélange dans la fabrication de sauces, de soupes, de plats cuisinés réfrigérés ou congelés et/ou de compositions alimentaires lyophilisées, tels que des produits à base de café soluble, par exemple. On peut ajouter le mélange selon l'invention dans une proportion de 0,07-0,50% par rapport au poids sec de la composition alimentaire, par exemple.

[0017] On peut chauffer la composition alimentaire aux microondes, en milieu aqueux ou à sec, dans un four conventionnel et/ou dans de l'eau bouillante, par exemple. Il se dégage alors une odeur prononcée de rôti ou une odeur prononcée de grillé.

[0018] La présente invention a enfin pour objet un mélange précurseur d'arômes, dans lequel la source de soufre non volatile comporte une ou plusieurs protéines contenant au moins un acide aminé soufré, de manière à permettre la formation d'une poche hydrophobe emprisonnant un ou plusieurs polysulfures sous forme d'un complexe, et permettant

ainsi de les protéger des altérations. On peut sécher ce complexe, de manière à obtenir une poudre aromatique stable. On peut notamment le sécher par pulvérisation ou par lyophilisation, par exemple.

[0019] La présente invention est décrite plus en détails à l'aide de tests et d'exemples non limitatifs, ci-après. Dans ces tests et dans ces exemples, les pourcentages sont donnés en moles sauf indication contraire.

**Test 1: Réaction entre du bis(2-furfuryl) disulfure et une source protéique comprenant au moins un groupe sulfhydryle**

[0020] On fait réagir, en milieu aqueux, à chaud, du bis(2-furfuryl) disulfure avec une source protéique, de manière à produire du 2-furfuryl-thiol isolé à l'aide d'un appareil de distillation-extraction simultanées, le SDE, à pression atmosphérique ou sous vide.

[0021] On calcule alors le rendement de formation de groupes thiols. Ce rendement est exprimé en pourcentage et est calculé sur la base de la quantité de groupes thiols qui devraient être formés, soit le double de la quantité molaire de disulfure.

[0022] L'ensemble de données est mentionné dans le tableau 1, ci-après.

Tableau 1

	(a)	Source protéique	Rendement	mode d'isolation
témoin		-	<1%	SDE/pression atmosphérique (100° C)
essai n°1	10 ppm	albumine d'oeuf	87%	SDE/pression atmosphérique (100° C)
essai n°2	10 ppm	albumine d'oeuf dénaturée	61%	SDE/pression atmosphérique (100° C)
essai n°3	10 ppm	albumine d'oeuf	<1%	SDE/sous vide (37° C)
essai n°4	100 ppm	gluten	45%	SDE/pression atmosphérique (100° C)
essai n°5	100 ppm	BSA	51%	SDE/pression atmosphérique (100° C)
essai n°6	100 ppm	$\beta$ -lactoglobuline	60%	SDE/pression atmosphérique (100° C)
essai n°7	1000 ppm	$\beta$ -lactoglobuline + 1% de cystéine	80%	SDE/pression atmosphérique (100° C)
essai n°8	100 ppm	hydrolysate de $\beta$ -lactoglobuline	20%	SDE/pression atmosphérique (100° C)
légende: (a) quantité de bis(2-furfuryl) disulfure / quantité de la source protéique				

[0023] Les résultats mentionnés au tableau 1 mettent en évidence le fait que la réaction, en milieu aqueux à chaud, entre un polysulfure, tel que le bis(2-furfuryl) disulfure, et une source protéique comprenant au moins un groupe sulfhydryle permet la formation de thiols correspondants, à un rendement intéressant.

Par ailleurs, l'essai n°3 permet de mettre en évidence le fait que si l'on fait réagir du bis(2-furfuryl) disulfure avec de l'albumine sous vide à température ambiante, aucun thiol correspondant n'est formé. Cela permet de confirmer le fait que le disulfure est complexé dans la poche hydrophobe formée par la protéine. On peut ainsi éviter la perte du polysulfure par évaporation et limiter la dispersion de son odeur avant le chauffage de la composition alimentaire à laquelle on a ajouté le mélange aromatique, selon l'invention.

Pour augmenter le rendement en thiol, on peut également former un complexe ternaire comprenant un disulfure, de la cystéine et une protéine, comme illustré à l'essai n°7.

**Test 2: Effet sur le rendement de la réaction de la quantité de polysulfure par rapport à la quantité de la source protéique contenant au moins un sulfhydryle**

[0024] On calcule le rendement de la réaction en fonction de la quantité de polysulfure par rapport à la quantité de la

source protéique contenant au moins un sulfhydryle.

[0025] Pour ce faire, on effectue plusieurs réactions, dans un milieu aqueux à chaud, avec, à chaque essai, une quantité croissante de bis(2-furfuryl)disulfure et une quantité constante d'albumine d'oeuf.

On calcule alors le rendement de formation de groupes thiols. Ce rendement est exprimé en pourcentage molaire et est calculé sur la base de la quantité de groupes thiols qui devraient être formés, soit le double de la quantité molaire de disulfure.

[0026] Les résultats sont mentionnés à la figure 1, ci-après.

[0027] La figure 1 met en évidence le fait que le taux de transformation du disulfure en furfurylthiol formé diminue quand le taux de bis(2-furfuryl)disulfure complexé dans la poche hydrophobe de la protéine augmente.

### Test 3: Réaction dans un milieu aqueux à chaud entre de l'albumine d'oeuf et différents polysulfures

[0028] On fait réagir, dans un milieu aqueux à chaud, de l'albumine d'oeuf avec différents polysulfures et l'on calcule le rendement de formation de thiol tel que décrit dans le test 1.

[0029] L'ensemble des résultats sont mentionnés dans le tableau 2, ci-dessous.

Tableau 2

	polysulfure	(a)	rendement	méthode d'isolation
essai n°9	bis(2-furfuryl) disulfure	10 ppm	87%	SDE/pression atmosphérique
essai n°10	bis(3-méthyl-2-buten-1-yl) disulfure	10 ppm	30%	SDE/pression atmosphérique
essai n°11	2-furfurylthiol	100 ppm	61%	SDE/pression atmosphérique
essai n°12	diméthyl trisulfure	10 ppm	7%	SDE/pression atmosphérique
légende: (a) quantité de polysulfure / quantité d'albumine d'oeuf.				

[0030] Les résultats mentionnés au tableau 2 mettent en évidence le fait que la réaction, en milieu aqueux à chaud, entre un polysulfure et une source protéique comprenant au moins un groupe sulfhydryle permet la formation de thiols correspondants.

[0031] Par ailleurs, ces résultats mettent en évidence le fait que cette réaction entre un polysulfure, le bis(2-furfuryl)disulfure, et une source protéique comprenant au moins un groupe sulfhydryle (essai n°9) permet la formation de thiols correspondants, à un rendement meilleur que dans le cas où l'on effectue une simple complexation entre un groupement thiol, le 2-furfurylthiol, et une source de protéines comprenant un groupement sulfhydryle (essai n°11). On peut supposer que cette différence de rendement est due au fait qu'il y a une réaction irréversible (essai n°11) entre le groupement thiol et la protéine avec formation de disulfures, des furfuryl-S-S-protéines, qui ne sont pas volatiles.

De plus, on n'a pas de perte de rendement lors de la réaction entre un polysulfure et une source protéique comprenant au moins un groupe sulfhydryle, car les thiols correspondants sont libérés au fur et à mesure de leur formation.

### Test 4: Acide aminé ou peptide comme source de soufre non volatile comprenant au moins un groupe sulfhydryle.

[0032] On fait réagir, dans un milieu aqueux à chaud, du bis(2-furfuryl)disulfure et un acide aminé ou un peptide, comme source de soufre non volatile comprenant au moins un groupe sulfhydryle. Le rapport massique bis(2-furfuryl)disulfure/source de soufre non volatile comprenant au moins un groupe sulfhydryle est de 1/10. On calcule alors le rendement de formation de thiol tel que décrit dans le test 1.

[0033] L'ensemble des résultats est mentionné dans le tableau 3, ci-dessous.

Tableau 3

	(b)	rendement	valeur du pH
essai n°13	cystéine	10-59%	-
essai n°14	cystéine	87%	7,6
essai n°15	glutathion	80%	7,6
essai n°16	cystine	2,8%	7,6
<u>Légende:</u> (b) source de soufre non volatile contenant au moins un groupe sulfhydryle ou un pont disulfure.			

**[0034]** Les résultats mentionnés au tableau 3 mettent en évidence le fait que le mélange de précurseur d'arômes selon la présente invention constitué d'un disulfure volatile, le bis(2-furfuryl)disulfure et d'un acide aminé soufré, la cystéine, ou d'un peptide contenant au moins un acide aminé soufré, le glutathion, permet la formation de thiols, lors d'une étape de chauffage en milieu aqueux, et ainsi génère une note aromatique.

Par contre, comme cela est illustré par l'essai n°16, si la source de soufre non volatile est une source de ponts disulfures, telle que la cystine, sans sulfhydryle libre, on obtient un rendement négligeable de formation de thiols. Les résultats mentionnés au tableau 3 mettent, de plus, en évidence le fait que la réaction est pH dépendante. En effet, si l'on fait réagir dans de l'eau distillée, à chaud, de la cystéine avec du bis(2-furfuryl)disulfure, comme à l'essai n°13, le rendement de formation de thiol varie entre 10 et 59%. Par contre si l'on effectue la même réaction dans de l'eau au pH de 7,6, comme dans l'essai n°14, on obtient un rendement de formation de thiols de 87%.

#### Test 5: Formation de thiols naturels

**[0035]** On produit par biotransformation des disulfides.

**[0036]** Pour ce faire, on met en suspension une levure boulangère dans un tampon phosphate à pH 8, contenant un conjugué cystéine-aldéhyde à 20 mM.

**[0037]** On effectue cette biotransformation pendant 48 h, pour la moitié de la préparation en milieu anaérobie et, pour l'autre moitié, en milieu aérobie, de manière à comparer l'effet de l'oxygène sur la formation de 2-furfurylthiol.

**[0038]** On mesure alors le rendement de la réaction. La formation de 2-furfurylthiol est à un rendement optimal de 30-40%, en milieu anaérobie, et à rendement optimal de 10-25%, en milieu aérobie.

**[0039]** Après 144 h d'incubation, on obtient la formation de bis (2-furfuryl) disulfure à un rendement optimal de 24% en milieu anaérobie et à un rendement optimal de 4% en milieu aérobie.

**[0040]** On fait alors réagir, en milieu aqueux, à chaud, le bis(2-furfuryl) disulfure naturel, ainsi préparé 144 h en conditions anaérobiques, avec de l'albumine d'oeuf, de manière à produire, à un rendement de 60%, du 2-furfurylthiol isolé à l'aide d'un appareil de distillation-extraction simultanées, le SDE, à pression atmosphérique.

#### Exemple 1

**[0041]** On procède à l'aromatisation de café soluble avec le mélange précurseur d'arômes selon l'invention, de manière à développer une note grillée très prononcée.

**[0042]** Pour ce faire, on fait réagir, à chaud dans 100 ml d'eau à pH 7,5, le mélange selon l'invention, comprenant 100 ppm de bis(2-furfuryl) disulfure et de la  $\beta$  lactoglobuline, avec 1,5 g de café soluble.

**[0043]** On obtient un mélange ayant un goût de café avec une note grillée très prononcée.

#### Exemple 2

**[0044]** On prépare un mélange précurseur d'arômes sous forme de poudre, pouvant être aisément utilisé pour donner une note aromatique prononcée aux aliments.

**[0045]** Pour ce faire, on forme un mélange précurseur d'arômes stable en mélangeant dans de l'eau 100 ppm de bis(2-furfuryl) disulfure avec de l'albumine. On effectue une lyophilisation du mélange précurseur d'arômes ainsi réalisé.

**[0046]** On obtient ainsi un mélange précurseur d'arômes sous forme de poudre que l'on peut facilement utiliser à sec, en suspension ou en solution, notamment, aux micro-ondes, de manière à ce qu'il développe une note aromatique grillée très prononcée.

### Exemple 3

[0047] On prépare un fond de sauce au jus de poulet rôti en y ajoutant le mélange selon l'invention.

[0048] Pour ce faire, on prépare un mélange précurseur d'arômes tel que décrit à l'exemple 2 et on l'ajoute à un fond de sauce à raison de 0,35% par rapport au poids sec de ce fond de sauce.

[0049] On obtient ainsi un fond de sauce au jus de poulet rôti ayant une note de viande très prononcée.

### Exemple 4

[0050] On prépare un hamburger en ajoutant dans le steak de viande hachée le système aromatique selon l'invention.

[0051] Pour ce faire, on prépare un mélange précurseur d'arômes tel que décrit à l'exemple 2 et on l'ajoute dans le steak à raison de 0,45% par rapport au poids sec du steak de viande hachée.

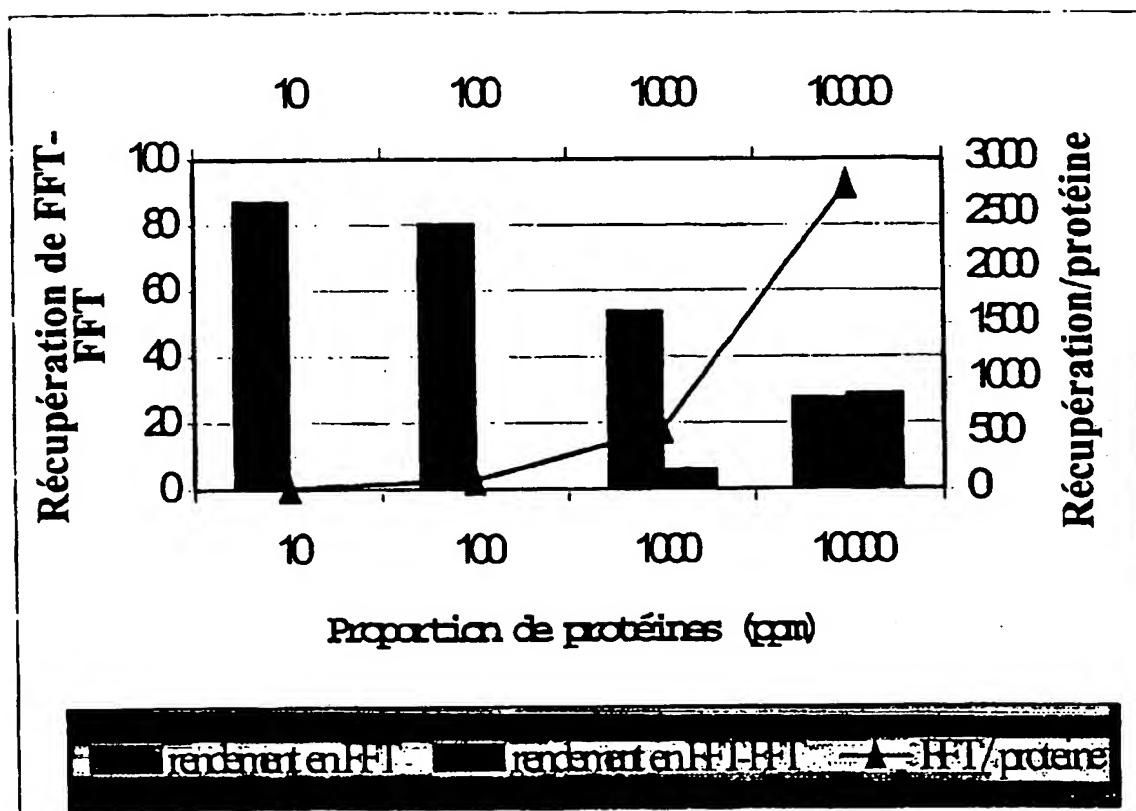
[0052] On dépose le steak ainsi préparé sur un demi pain rond avec une garniture composée de salade, de tomates et de cornichons coupés en rondelles, puis on superpose l'autre portion du pain rond.

[0053] On obtient ainsi un hamburger ayant une note de viande très prononcée, lors de la réchauffe aux micro-ondes.

### Revendications

1. Mélange précurseur d'arômes caractérisé par le fait qu'il génère, lors d'une étape de chauffage une note aromatique due à la formation de thiols.
2. Mélange selon la revendication 1, caractérisé par le fait qu'il est constitué d'un polysulfure et d'une source de soufre non volatile comprenant au moins un groupe sulfhydryle.
3. Mélange selon les revendications 1 et 2, dans lequel le polysulfure est de type  $R-(S)_n-R'$  où R et R' sont identiques ou différents et n est supérieur ou égal à 2.
4. Mélange selon les revendications 1 à 3, dans lequel le polysulfure est obtenu par biotransformation d'un conjugué cystéine-aldéhyde à l'aide d'une levure boulangère.
5. Mélange selon les revendications 1 à 4, dans lequel la source de soufre non volatile combinée ou non à d'autres constituants, est un acide aminé soufré, un peptide contenant au moins un acide aminé soufré, une protéine contenant au moins un acide aminé soufré et/ou un hydrolysate de protéines contenant au moins un acide aminé soufré.
6. Mélange selon les revendications 1 à 5, dans lequel la formation de thiol est à un rendement de 48-90%, lors d'une étape de chauffage à pH neutre.
7. Mélange selon l'une des revendications 1 à 6, dans lequel la source de soufre non volatile est une ou plusieurs protéines comprenant au moins un acide aminé soufré, de manière à permettre la formation d'une poche hydrophobe emprisonnant un ou plusieurs polysulfures.
8. Mélange selon la revendication 7, caractérisé par le fait qu'on le sèche, de manière à obtenir une poudre aromatique stable.
9. Utilisation du mélange selon l'une des revendications 1 à 8 dans la fabrication d'une composition alimentaire, de manière à favoriser le développement d'une note aromatique rôtie, grillée lorsqu'on chauffe la composition alimentaire.
10. Utilisation selon la revendication 9, dans laquelle on ajoute le mélange aromatique dans une proportion de 0,07-0,50% par rapport au poids sec de la composition alimentaire.





**Légende:** - FFT: 2-furfurylthiol  
 - FFT-FFT: bis (2-furfuryl) disulfure



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## RAPPORT DE RECHERCHE EUROPEENNE

Numéro de la demande  
EP 98 20 1490

DOCUMENTS CONSIDERES COMME PERTINENTS			
Catégorie	Citation du document avec indication, en cas de besoin, des parties pertinentes	Revendication concernée	CLASSEMENT DE LA DEMANDE (Int.Cl.6)
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Lieu de la recherche <b>LA HAYE</b>		Date d'achèvement de la recherche <b>16 décembre 1998</b>	Examineur <b>Van Moer, A</b>
CATEGORIE DES DOCUMENTS CITES		T : théorie ou principe à la base de l'invention E : document de brevet antérieur, mais publié à la date de dépôt ou après cette date D : cité dans la demande L : cité pour d'autres raisons & : membre de la même famille, document correspondant	
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## RAPPORT DE RECHERCHE EUROPEENNE

Numéro de la demande  
EP 98 20 1490

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Catégorie	Citation du document avec indication, en cas de besoin, des parties pertinentes	Revendication concernée	CLASSEMENT DE LA DEMANDE (Int.Cl.6)
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Le présent rapport a été établi pour toutes les revendications			
Lieu de la recherche <b>LA HAYE</b>		Date d'achèvement de la recherche <b>16 décembre 1998</b>	Examineur <b>Van Moer, A</b>
<p><b>CATEGORIE DES DOCUMENTS CITES</b></p> <p>X : particulièrement pertinent à lui seul Y : particulièrement pertinent en combinaison avec un autre document de la même catégorie A : arrière-plan technologique O : divulgation non-écrite P : document intercalaire</p> <p>T : théorie ou principe à la base de l'invention E : document de brevet antérieur, mais publié à la date de dépôt ou après cette date D : cité dans la demande L : cité pour d'autres raisons &amp; : membre de la même famille, document correspondant</p>			

EPO FORM 1503 03 92 (P4/C02)

**ANNEXE AU RAPPORT DE RECHERCHE EUROPEENNE  
RELATIF A LA DEMANDE DE BREVET EUROPEEN NO.**

EP 98 20 1490

La présente annexe indique les membres de la famille de brevets relatifs aux documents brevets cités dans le rapport de recherche européenne visé ci-dessus.  
Lesdits membres sont contenus au fichier informatique de l'Office européen des brevets à la date du  
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16-12-1998

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Pour tout renseignement concernant cette annexe : voir Journal Officiel de l'Office européen des brevets, No.12/82





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3,421,906

## COFFEE STABILIZATION

Ismar M. Reich, Stamford, Conn., and Alexander S. Cascione, Yonkers, N.Y., assignors to Coffee Instants, Inc., a corporation of New York  
No Drawing. Filed Sept. 3, 1964, Ser. No. 394,323  
U.S. Cl. 99—152 2 Claims  
Int. Cl. A23f 1/04; A23f 1/06

### ABSTRACT OF THE DISCLOSURE

Stabilization of the flavor and aroma of processed coffee products without introducing objectionable aromas and flavors so that the desirable quality of freshly roasted coffee may be retained. The processed coffee having vapors of a stabilizing agent providing sulfur dioxide associated therewith and vapors of ammonia so that any acrid odor resulting from the sulfur dioxide is reduced to a tolerable level.

This invention relates to a method for treating roasted coffee to retard staling.

Green unroasted coffee is relatively stable and may be stored for extended periods, even for a year or more exposed to air, without serious loss of quality. The flavor and aroma of coffee is developed only when it is roasted. After roasting, the coffee is very unstable when exposed to air. It is established that exposure of roasted coffee to oxygen, produces stale, objectionable flavors and aromas. The staleness is not rancidity but is apparently a result of the alteration of the compounds which contribute to the desirable characteristics of coffee.

A very considerable effort and cost is expended in order to preserve roasted coffee by means of protective packages. These range all the way from tins in which coffee is packaged, initially under a vacuum obtained by exhausting the air and its associated oxygen, to cellophane packages. The various packages afford varying degrees of protection and stability to the product. The tin container, whether initially under vacuum or whether purged with an inert gas, maintains the product essentially without change. However, there is opportunity for contact with air prior to packaging which results in some loss of quality. In addition, following opening of the container by the consumer, a rapid rate of staling commences. Thus, even the relatively expensive tins that are widely used do not completely preserve the product until it is consumed. Less efficient packages such as cellophane or plastic containers permit some oxygen entry to the package and there is a corresponding staling which occurs at a rate related to the permeability of the package, even when the package remains intact.

It is well-known that ground, roasted coffee is less stable than whole bean roasted coffee. Similarly, a fine grind of roasted coffee is less stable than a medium or coarse grind. The stability also appears to be related to the moisture content of the roasted coffee, stability being poorer at higher moisture levels.

Thus, the stability problem is particularly important in marketing ground roasted coffee which has had a small quantity of moisture added as a practical means of stopping the roasting process and avoiding burning of the coffee.

A similar problem exists in instant coffee which has been "aromatized" by the addition, for example, of a small percentage of finely ground roasted coffee, or by the addition of oil obtained from roasted coffee. In instant coffee there is a much greater surface area exposed to the air. Market requirements for the bulk density of instant coffee are such that almost 80% of the volume of the final container is gas. Even when packaged in inert gas, it is not commercially feasible to eliminate all oxygen

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from the container, and exposure to air is severe following opening of the container. Furthermore, there is in general a much lower total level of aroma in instant coffee than in regular roasted coffee. The grinding process, also in most cases results in extensive exposure of coffee to air.

Other methods have been suggested for providing means for stabilization of ground coffee such as by the addition of an anti-oxidant either in gaseous or solid form. Such means is disclosed in U.S. Patent No. 1,956,290 entitled "Preparation of Coffee" granted on April 24, 1934.

The above patent discloses the use of certain salts which, when added to ground coffee, release a gaseous vapor such as sulfur dioxide to stabilize the ground coffee. Also suggested is the use of sulfur dioxide vapors. When the salts are used, it has been found that the generation of sulfur dioxide occurs at a relatively slow rate and has only a small effect in stabilizing the coffee aroma. When sulfur dioxide is used, an objectionable acrid aroma is present due to the presence of sulfur dioxide vapor. Furthermore, salts that will generate a sulfur dioxide atmosphere such as potassium sulfite, potassium bi-sulfite or the like, on prolonged contact with roasted coffee, release very objectionable levels of sulfur dioxide from the standpoint of acrid aroma while failing to provide significant protection or stabilizing the coffee to maintain the fresh coffee aroma.

An object of our invention is to stabilize the coffee flavor and aroma without introducing objectionable aromas and flavors, so that the desirable quality of freshly roasted coffee may be retained and provided to the consumer. Another object of our invention is to provide means for coffee stabilization and to prevent staling thereof before the product is packaged, during the storage of the product if the package is not impervious to oxygen, and especially after opening the packaged product and until it is completely used by the consumer. This invention applies to whole bean as well as ground roasted coffee.

A further object of our invention is to stabilize finely ground roasted coffee for admixture with instant coffee (which is dried, aqueous extract of roasted coffee) to improve flavor and provide a fresh coffee aroma for the instant coffee, so that aromatized coffee is superior both in quality and stability to any heretofore available. Still another object of our invention is to provide an inexpensive method of stabilizing roasted coffee in which the coffee maintains the fresh flavor and aroma of freshly roasted coffee for protracted periods until consumed and which, by the addition of adjuvants to stabilize the coffee, does not have an objectionable acrid odor.

Our invention contemplates providing a stabilized coffee product and method in which the addition of adjuvants to fresh roasted coffee will maintain the fresh flavor and aroma of the coffee. Thus, treating roasted coffee in the presence of gaseous vapors and thereafter packaging the treated coffee will stabilize the flavor and aroma inherent of coffee and in which the gaseous vapors will not add an objectionable acrid odor by their presence.

A further objective is to stabilize roasted coffee oil, which may be obtained either by expelling by means of pressure applied to roasted coffee or by solvent extraction of roasted coffee. Such oils may be added to instant coffee to provide improved flavor and aroma. Another objective is to stabilize finely ground roasted coffee for a use as a flavoring in ice cream, baked goods, etc.

It has been found that the tendency of roasted coffee to become stale on exposure to air is retarded greatly by contact of the coffee with sulfur dioxide vapor. Low levels of absorption are effective over a range of levels of absorbed sulfur dioxide. The higher the level, a reduction of the rate of staling of the coffee on exposure to air occurs. However, the odor of sulfur dioxide is readily detectable and is irritating and objectionable. It is de-

tectable by the average person at 0.3 to 1 part per million in the air. The irritating character of its odor, even at low levels, prevents its effective use as a coffee flavor and aroma stabilizer. When the level of sulfur dioxide is reduced sufficiently to avoid the objectionable odor, the effectiveness of its use is correspondingly reduced.

We have discovered that the objectionable odor and flavor of coffee exposed to levels of sulfur dioxide effective as a flavor and aroma stabilizer can be eliminated without harm to the desirable aroma and flavor of the coffee by the addition of ammonia vapor at substantially the same time the coffee is treated with sulfur dioxide vapors.

Ammonia is also irritating and its odor is detectable at a level of 53 parts per million in air. However, our invention employs both vapors at controlled and substantially low yet effective levels, with the unexpected result, that the stabilization effect of sulfur dioxide is not inhibited while its irritating odor is eliminated. The use of this invention provides improved roasted coffee products to the consumer regardless of the type of packaging used. However, when the ground coffee or instant coffee product containing ground roasted coffee is stored in a hermetically sealed container free of oxygen a greatly improved product becomes available to the consumer, particularly, in regard to the very low rate of staling following opening of the container. We have found that preferred levels of sulfur dioxide may range from approximately 0.02% to 0.40% based on the weight of roasted coffee having an irritating and acrid aroma. As indicated, we have overcome these objectionable odors by using vapors of ammonia. We have found that ratios of ammonia vapors to sulfur dioxide vapors of approximately 0.65 to 2.0 are effective in eliminating the irritating and acrid odor of sulfur dioxide vapors. At these levels, ammonia vapor was not detectable to any substantial or intolerable degree. Of importance is the fact that the use of such vapors does not cause undesirable loss of flavor when the coffee is brewed. Ratios below about 0.65 are not effective in preventing the acrid aroma. On the other hand, ratios above about 2.0 result in an objectionable odor caused by excess ammonia.

The preferred method of carrying out our invention is to introduce anhydrous sulfur dioxide vapor continuously directly into the grinding chamber of the mill used to grind roasted coffee. Ammonia vapor is fed into the conduit through which the ground, roasted coffee passes as it leaves the grinding chamber. The flow of both vapors can be easily controlled by means of flow regulators and indicators. Both vapors are available commercially as highly purified products in the form of anhydrous liquids under pressure.

Alternative procedures which also are effective include feeding of both vapors directly to the grinding chamber, or even the feeding of the ammonia first and followed by the sulfur dioxide.

Analytical data indicate that a major proportion of the vapors used is retained by the roasted coffee when the preferred method is employed with cooling during grinding.

It is known that at least a major part of the desirable coffee aroma compounds reside in oil present in the coffee. This oil comprises approximately 15% of roasted coffee. It is also known that both sulfur dioxide and ammonia are highly soluble in this oil. It is believed from consideration of the chemistry of the sulfites, that they would be insoluble in coffee oil. Furthermore the sulfites, being solids, would not have access to much of the roasted coffee oil which, even in very fine grinds of coffee, is largely occluded within the coffee particles. Unlike solids, vapors appear to penetrate the coffee particles and reach the coffee oil so that they can be stabilized. The protection to the fresh aroma of roasted ground coffee afforded by the present invention is applicable to mixtures of coffee so treated with other foods. For example, at a level

of 0.2% sulfur dioxide on a roasted coffee solids basis and 0.26% ammonia on a roasted coffee solids basis, finely ground roasted coffee was added to instant coffee at a level of 5% of the mixture. The aroma stability was greatly improved as compared to controls tested. The prepared controls were a sample of ground roasted coffee without vapors of sulfur dioxide and ammonia. A second sample was ground which contained finely ground ammonium sulfite at a level to provide the same level of sulfur dioxide equivalent to that of the standard procedure sample. A third sample was the same as the second sample except that ammonia vapor was also added at a level to bring the total ammonia equivalent to that in the standard sample. The sample with the salt alone was both acrid and stale although not as stale as the untreated sample. The sample with added ammonia vapor to the salt was not acrid but was about as stale as the sample with the salt alone. The samples were packed in jars without the removal of the air present. Yet, were the total amount of sulfur dioxide present to be oxidized to sulfate by the oxygen in the air, it would consume only about 3% of the oxygen present in the jar.

The following are examples illustrating the treatment of roasted coffee according to our invention:

#### Example I

A blend of Colombian and Costa Rican coffees, conventionally roasted to a medium roast color, is used. This coffee is fed to a Fitzpatrick Model D comminuting machine, manufactured by The W. J. Fitzpatrick Co., Chicago, Ill., at a rate of 190 pounds per hour. The Fitzpatrick mill, with a 10 horsepower motor, is equipped with liquid carbon dioxide cooling to facilitate fine grinding and prevent rapid oxidation of the coffee due to oxygen in air. The mill is operated at a speed of 6960 r.p.m. and is fitted with a 50 mesh screen so that all the coffee is ground finer than 50 mesh. Anhydrous sulfur dioxide is fed into the grinding chamber by means of a tube which penetrates the housing of the mill. The flow rate is controlled by means of a pressure reducing valve, needle valve, and rotameter attached to a cylinder containing liquefied anhydrous sulfur dioxide. The flow rate is maintained at 0.031 s.c.f.m. Anhydrous ammonia is fed similarly except that it is introduced at a rate of 0.157 s.c.f.m. at a point just after the coffee has been ground and has passed through the screen. The finely ground treated coffee is mixed with instant coffee, in batches of 700 pounds, at a ground coffee level of 5% of the mixture. The instant coffee had been purged by passing carbon dioxide gas vertically upward through a bed of the instant coffee until the exiting was analyzed 2% oxygen before mixing with the ground roasted coffee. The mixture is then packaged in glass jars using conventional packaging equipment equipped with carbon dioxide purging. The jars are sealed with metal caps provided with glued glassine inner seals conventionally used as moisture barriers. The packaged product was compared with similarly packaged competitive "aromatized" instant coffee including samples containing finely ground roasted coffee with instant coffee and samples containing coffee oil with instant coffee. Also control samples similarly prepared as stated above were examined. The initial evaluation indicated that all samples were comparable in quality although differing somewhat in character. On re-examination three days after opening the jars, however, the sample treated with sulfur dioxide and ammonia was found to be far superior to all the others in aroma and flavor. These subjective examinations carried out even as long as several weeks showed that the flavor and aroma of the sulfur dioxide and ammonia treated sample was preserved though somewhat diminished while the other samples had become stale.

#### Example II

The same procedure as in Example I was followed for grinding and treating the roasted coffee with increased



levels of sulfur dioxide vapors. In this connection, the level of sulfur dioxide vapors was increased to 0.33% based on the weight of roasted coffee. The ammonia to sulfur dioxide ratio of that in Example I remained constant.

The coffee was evaluated as in Example I. The aroma was good but there was a small loss of the fresh flavor. When compared with the comparative samples used in Example I, the flavor and aroma of the coffee was better and did not become stale as fast. However, the sample according to Example I tasted slightly better.

### Example III

Approximately 50 grams of freshly roasted coarsely ground coffee of approx. 10 mesh is placed in a jar of about 240 ml. capacity. A glass tube is inserted with its outlet near the bottom of the jar. The other end of the tube is connected to a cylinder of liquefied anhydrous sulfur dioxide equipped with a flow regulator and indicator. Sulfur dioxide vapor is fed for a period of 15 minutes at a rate of about 2.0 cubic feet per hour. Following this a tube is similarly connected to a cylinder of liquefied anhydrous ammonia which is fed at a rate of about 3.9 cubic feet per hour for 20 seconds. A small sub-sample is taken after the sulfur dioxide flow and before the ammonia flow and is compared with a sample of untreated ground roasted coffee and with the coffee treated with both vapors.

The pH values of brews made by pouring 6 oz. of boiling water on 5 grams of coffee is measured after the brews are cooled.

Sample:	pH
Untreated control	5.10
Treated with SO <sub>2</sub>	5.00
Treated with SO <sub>2</sub> and with NH <sub>3</sub>	5.18

To determine the quantity of sulfur dioxide absorbed, samples of coffee brews made in the same way were titrated with dilute sulfuric acid. The titration data indicates that the pH is linear between about pH 4.5 and 5.5 with added acid and the equivalent of 0.0475% sulfur dioxide by weight based on the roasted coffee lowers the pH by 0.1 unit. Thus measurement of pH changes of brews affords an approximate determination of the amount of sulfur dioxide added. Similarly, the approximate ammonia level retained may be calculated. In the above example, it is estimated that the level of added sulfur dioxide is about 0.05%. In the above example, carried out at room temperature, a very large excess of sulfur dioxide is used as compared to that retained. In other experiments with lower temperatures, more efficient contact and mixing, as when the vapor is injected directly into the grinder during grinding, and with finer grinds, the retention of sulfur dioxide is much more efficient, most of the added vapor being retained by the coffee. In the case of ammonia, on the other hand relatively much more of the vapor used is retained, even under the same conditions of contact where the sulfur dioxide retention is inefficient.

Additional samples were prepared in the same manner as indicated above. The calculated retained sulfur dioxide is tabulated below along with evaluation of the relative quality of the samples after storage in air for two days.

Sample	Initial pH	pH after SO <sub>2</sub> treatment	pH after NH <sub>3</sub> treatment	Calculated, percent SO <sub>2</sub> retained	Evaluation
1	5.20	(1)	(1)	0	Stale.
2	5.10	5.00	5.18	0.05	Acceptable.
3	5.20	5.00	5.31	0.10	Good.
4	5.20	4.80	5.20	0.20	Very good.

<sup>1</sup> No treatment.

The finely ground coffee as set forth in Examples I and II was discharged from the mill at a temperature of approximately minus 50° C. The level of sulfur dioxide used was approximately 0.16% by weight based on the coffee; that of the ammonia approximately 0.21%.

Other methods for providing the sulfur dioxide and ammonia vapors to the roasted coffee will be apparent to those skilled in the industry. These could include the chemical generation of the vapors separate from or even in contact with the coffee.

It is apparent that modifications and changes can be made without departing from the scope of our invention as defined in the appended claims.

We claim:

1. A method of substantially eliminating the acrid odors present in a processed coffee product treated with sulfur dioxide comprising: exposing the coffee to vapors of sulfur dioxide in an amount of approximately 0.02% to 0.4% based upon the weight of the processed coffee, to stabilize the quality thereof and exposing said coffee to vapors of ammonia, the ratio by weight of ammonia to sulfur dioxide being about 0.65 to 2.0, so that any acrid odor resulting from the sulfur dioxide is reduced to a tolerable predetermined level.

2. A processed coffee product produced according to the process of claim 1.

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MAURICE W. GREENSTEIN, *Primary Examiner*.

U.S. Cl. X.R.

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## COFFEE FLAVOR ENHANCER

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U.S. Cl. 99—71

9 Claims

### ABSTRACT OF THE DISCLOSURE

The flavor of soluble coffee is improved in the direction of freshly roasted and ground coffee by addition of a small but effective amount of methyl mercaptan to an aqueous extract of soluble coffee solids prior to drying the extract to a stable moisture content.

### BACKGROUND OF THE INVENTION

This invention relates to enhancing the flavor of soluble coffee by addition of a known compound to the coffee percolate prior to drying.

The art of aromatizing soluble coffee by direct addition of volatile aromas to the dry coffee itself (via plating with coffee oil) as well as indirect addition of volatile aromatics to the soluble coffee extract prior to co-drying the aromas and extract have not met with great success. Plating causes flavor stability problems, spray-drying of aromatized extract allows important volatiles to evaporate or "flash-off" and generally unbalances the coffee flavor while freeze-drying the aromatized extract is very expensive. Moreover, even freeze-dried soluble coffee while having improved retention of volatiles does not taste exactly like freshly roasted and ground coffee and is found to contain some unbalanced flavor notes.

In lieu of the above, it has long been desired to find a simple method for enhancing coffee flavor which would include addition of one or more known compounds to either the dry soluble coffee itself or to the liquid coffee percolate prior to the drying step. This invention relates to the latter technique of simple addition of such a compound to the extract and then drying said extract.

### SUMMARY OF THE INVENTION

This invention is founded on the discovery that the flavor of soluble coffee can be enhanced by simple addition of a small but effective amount of methyl mercaptan to the aqueous coffee percolate (obtained from a conventional extraction train) prior to drying. The drying method is not critical as long as some form of heat is applied in removal of the water from the extract and can include conventional spray-drying (at air temperatures of 500° F. or above), low temperature spray-drying techniques (at air temperatures below 500° F.), as well as freeze-drying techniques under vacuum or atmospheric conditions.

### DETAILED DESCRIPTION OF THE INVENTION

Methyl mercaptan ( $\text{CH}_3\text{SH}$ ) is a known compound, the synthesis of which is described in the chemical literature and which is readily available commercially.

The level of methyl mercaptan which is added to the coffee extract can vary between  $5 \times 10^{-4}$  and  $1 \times 10^{-9}$  parts of methyl mercaptan by weight of soluble coffee solids. At concentrations of less than  $1 \times 10^{-9}$  parts, there is no noticeable enhancement of flavor upon drying the extract, while at concentrations of above  $5 \times 10^{-4}$  parts, the methyl mercaptan's own flavor becomes noticeable and detracts from the enhancement.

A preferable level of methyl mercaptan has been found to be 1 to 500 parts per million (p.p.m.). When freeze-

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drying coffee extract, preferable level of methyl mercaptan has been found to be 1 to 30 p.p.m. When spray-drying said extract (at 500° F.) the level of methyl mercaptan is preferably increased to between 30 to 300 p.p.m. The level of methyl mercaptan can be lowered to 20 to 100 p.p.m. by lowering the spray-drying temperature of below 500° F., say 100° to 300° F. Also, higher levels of methyl mercaptan can be used in drying provided that the enhanced product is mixed with an appropriate amount of dry solids containing no methyl mercaptan to achieve the desired cup solids level.

Enhancement can be achieved by simple addition of the desired level in the coffee extract and then drying said extract by the application of heat. It may be preferred to add the desired level of mercaptan to a portion of extract, dry this enhanced portion, and then blend this dried extract with the dry solids containing no mercaptan. The methyl mercaptan can be added to the extract in the form of a dilute alcohol or water solution. Moreover, the heat applied during drying need not be excessive since conventional vacuum freeze-drying wherein the product temperature never exceeds 80° to 100° F. is capable of achieving good roasted coffee flavor in the final soluble coffee. Likewise, conventional spray-drying techniques wherein the atomized extract is exposed to temperatures as high as 500° to 600° F. or above for fractions of a second also attains enhancement. Finally, spray-drying the extract under low temperature drying conditions of between 100° to 300° F. also achieves an unexpected enhancement of roasted coffee flavor.

While the mechanism of the particular flavor development is not known, it is theorized that the methyl mercaptan chemically or physically reacts with organic chemical compounds naturally present within the soluble coffee solids in a time-temperature-solids concentration relationship to give an unexpected product in the direction of roasted coffee flavor upon drying of the extract. Unexpectedly, this reaction is not achieved when the methyl mercaptan is simply added to coffee which is not dried or heated, e.g., added directly to dried coffee solids or a cup of reconstituted coffee.

In addition to methyl mercaptan alone affecting flavor enhancement of roasted and ground coffee extract solids, methyl mercaptan also acts in combination with other compounds, such as diacetyl, to effect a desirable flavor change.

### PREFERRED EMBODIMENTS OF THE INVENTION

This invention will now be described by reference to several specific examples which are believed to more clearly describe this invention.

#### Example 1

Coffee percolate having an extract concentration of 30% soluble solids was obtained from a series of percolation columns in the conventional manner. Methyl mercaptan was then added to this extract to give 3 p.p.m. (parts per million) of methyl mercaptan on a soluble solids basis. The aromatized extract was then fed to a co-current spray-drying tower having a 12' diameter, a drying zone of about 18' in height and an overall tower height of about 45'. The coffee was atomized under suitable pressure conditions to a maximum particle size of between 250 and 300 microns. Inlet temperature was between 500° and 550° F., outlet temperature was 240° to 255° F., and the particles had a residence time of between 10 to 20 seconds before the heated air exited from the dryer. The dried coffee had a moisture content of about 3% and a density of 0.25 g./cc.

The enhanced soluble coffee reconstituted to give an "instant" coffee which was difficult to distinguish from a control sample prepared in the same manner which

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did not contain methyl mercaptan. However, when the level of methyl mercaptan was increased to 40 p.p.m. on a soluble solids basis (and the extract dried) a distinct improvement in the direction of a freshly roasted coffee flavor preferred by many individuals was perceived. This roasted coffee flavor note was more evident as the level of mercaptan compound was increased to 66 p.p.m. (soluble solids basis). At 132 p.p.m., the enhancement was even more evident, and still desirable. At levels of above 300 p.p.m., on a soluble solids basis, sulfide note giving an off-taste to the coffee were noted. However, the coffee solids containing 300 p.p.m. methyl mercaptan were then mixed with coffee solids which contained no mercaptan to thereby lower the level of methyl mercaptan on a cup solids basis to the 40-66 p.p.m. level. This gave a desirable flavor enhancement in the reconstituted cup.

#### Example 2

The coffee percolate of Example 1 (with 3 p.p.m. methyl mercaptan added on a soluble solids basis) was spray-dried under more gentle drying conditions. Chamber dimensions were 3' in diameter and drying height was 4'. The coffee extract was fed to an atomizing bowl having a downwardly directed liquid feed at a rate of 1.5 to 2.0 gallons per hour and was dried by air having an inlet temperature of 310° to 355° F. and an outlet temperature of 150° to 175° F. The drying air entered the chamber in a counter-current fashion and then reversed its direction and exited from the drying chamber in a co-current fashion along with the dried coffee powder.

Enhancement of this product when compared to a control sample (not having added methyl mercaptan) was not evident. Enhancement was not noted until levels of 20 p.p.m. were reached. However, at levels of 40 to 66 p.p.m. enhancement was more evident than in the Example 1 product at the same levels. Here also, at levels above 300 p.p.m., off-tastes in the reconstituted coffee were noted but were off-set by dry-blending the enhanced coffee with coffee solids which contained no mercaptan.

#### Example 3

The coffee percolate of Example 1 (with 3 p.p.m. of methyl mercaptan added on a soluble basis) was frozen to below its eutectic freezing point (-13° F.), ground, and then vacuum freeze-dried in apparatus similar to that shown in Abbott et al. 3,132,930, at a pressure of below 200 microns to achieve a final moisture content of 2.5% while avoiding product temperatures in the dried extract which exceeded 100° F.

This product, when compared to a control freeze-dried without mercaptan, had desirable fresh roasted coffee flavor notes preferred by most people.

The level of methyl mercaptan was varied in this example between 3 p.p.m. and 9 p.p.m. to obtain a distinct and desirable enhancement in the direction of roasted coffee flavor notes. However, at levels of 30 p.p.m. a slight off-taste was perceived which was more evident at levels of 127 p.p.m. and 193 p.p.m. Here also, this could be off-set by dry-blending with coffee solids containing no mercaptan.

#### Example 4

Various levels of methyl mercaptan were added directly (without co-drying) to various reconstituted cups of coffee (including spray-dried soluble coffee, freeze-dried soluble coffee, and fresh percolate). In all cases, no enhance-

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ment of coffee flavor was detected but, on the contrary, an undesirable mercaptan or sulfide taste could be perceived. This was evident at the 10 p.p.m. level (solids basis) and increased in proportion to the level of mercaptan added. In no case was a desirable enhancement or improvement in coffee flavor noted.

While this invention has been described by reference to specific examples, it is understood to be limited only by the scope of the appended claims.

What is claimed is:

1. A method of imparting roasted coffee flavor to soluble coffee which comprises adding a small but effective amount of methyl mercaptan to an aqueous extract of roasted coffee solids and then drying said extract to a stable moisture content by application of heat during at least a portion of the water removal process.

2. The process of claim 1 wherein the methyl mercaptan is added to the extract at a level of between  $5 \times 10^{-4}$  to  $1 \times 10^{-9}$  parts of mercaptan for each part of soluble coffee solids (dry basis).

3. The process of claim 1 wherein the methyl mercaptan is added to the extract at a level of between 1 to 500 parts per million (p.p.m.) of mercaptan for each part of soluble coffee solids.

4. The process of claim 3 wherein the methyl mercaptan is added to the extract at a level of between 1 to 30 p.p.m. and the extract is freeze-dried under vacuum conditions of less than 500 microns.

5. The process of claim 3 wherein the methyl mercaptan is added to the extract at a level of 30 to 300 p.p.m. and the extract is spray-dried at air temperatures of above 500° F.

6. The process of claim 3 wherein the methyl mercaptan is added at a level of 20 to 100 p.p.m. and the extract is spray-dried at air temperatures of below 500° F.

7. The process of claim 4 wherein the extract is divided into two portions, the methyl mercaptan is added to only one portion of the extract, both portions are dried, and then dry-blended to achieve the desired level of mercaptan on a dry basis.

8. The process of claim 5 wherein the extract is divided into two portions, the methyl mercaptan is added to only one portion of the extract, both portions are dried, and then dry-blended to achieve the desired level of mercaptan on a dry basis.

9. The process of claim 6 wherein the extract is divided into two portions, the methyl mercaptan is added to only one portion of the extract, both portions are dried, and then dry-blended to achieve the desired level of mercaptan on a dry basis.

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TIM R. MILES, Primary Examiner

R. HALPER, Assistant Examiner

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Scarpellino et al.

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[45] Mar. 29, 1983

[54] METHOD FOR PRODUCING PRODUCTS  
ENHANCED WITH SYNTHETIC COFFEE  
GRINDER GAS FLAVOR

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## Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 195,913, Oct. 10, 1980,  
abandoned, which is a continuation of Ser. No. 15,988,  
Feb. 28, 1979, abandoned, which is a continuation of  
Ser. No. 906,811, May 17, 1978, abandoned.

[51] Int. Cl.<sup>3</sup> ..... A23L 1/234

[52] U.S. Cl. .... 426/533; 426/534;  
426/594

[58] Field of Search ..... 426/533, 534, 594

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[57]

## ABSTRACT

Known coffee flavor compounds including methyl mercaptan, a molar excess of carbonyl compounds and furfuryl mercaptan are combined in an aqueous solution of an inert, water-soluble carbohydrate at a preferred level of less than about 3% and then promptly dried, such as by spray-drying. These compounds may be fixed either separately or together. The dried fixed enhancer material is then combined with soluble coffee solids and/or soluble coffee-like solids powdered food-stuffs.

14 Claims, No Drawings

# METHOD FOR PRODUCING PRODUCTS ENHANCED WITH SYNTHETIC COFFEE GRINDER GAS FLAVOR

This application is a continuation-in-part of Ser. No. 195,913 filed Oct. 10, 1980 which application was in turn a continuation of Ser. No. 15,988, filed Feb. 28, 1979, which was a continuation of Ser. No. 906,811, filed May 17, 1978, all of which are now abandoned.

## BACKGROUND OF THE INVENTION

The present invention relates to the preparation of powdered coffee-flavored foodstuffs as well as soluble coffee powders, soluble coffee-like powders and combinations thereof which, when reconstituted, possess the flavor and/or aroma characteristics of roasted and ground coffee. According to this invention the term, "powdered coffee-flavored foodstuff" is meant to include products which are not regarded as coffee substitutes and are designed to be dissolved in a hot or cold aqueous fluid such as milk or water to produce a coffee-flavored food or beverage. Typical coffee-flavored food powders included powder creamers, powdered soft drink mixes, powdered pudding mixes and powdered gelatin dessert mixes. The term "soluble coffee-like powders" is meant to include those products which are useful as soluble coffee substitutes and which are comprised of soluble solids obtained from roasted vegetable material such as chicory, wheat, barley, chickpeas and others known to those skilled in the art. More particularly this invention relates to a synthetic coffee grinder gas aroma which is an improvement over the grinder gas aroma disclosed in commonly-assigned U.S. Pat. No. 3,852,481 to Feldman et al. This invention is also concerned with methods of fixing coffee flavor and aroma enhancers as well as combining the fixed enhancers with a powdered foodstuff, a soluble coffee powder and/or a soluble coffee-like powder.

According to the aforementioned Feldman et al. patent, which is hereby incorporated by reference, a synthetic grinder gas aroma is produced by combining methyl mercaptan along with certain aldehydes and ketones and then combining this aroma mixture with an edible carrier such as coffee oil or with soluble coffee. The synthetic grinder gas aroma produced according to the Feldman et al. patent constituted a significant advance in the art of soluble coffee enhancement; however, the Feldman aroma has been considered lacking in certain aroma flavor notes, most notably a roasted note, which are found in natural grinder gas aroma.

## SUMMARY OF THE INVENTION

The present invention relates to a composition which will provide a coffee grinder gas aroma comparable to that of natural coffee grinder gas and including a desirable roasted note. This invention also relates to a technique for fixing the new composition in a manner which avoids significant deterioration of desirable flavor notes and in a manner which permits the fixed composition to be combined with soluble coffee or coffee-like powders, a powdered foodstuffs to which it is desired to add or enhance a coffee flavor.

According to this invention, methyl mercaptan is contacted with a mole excess of a mixture of carbonyl compounds including acetaldehyde, a four or five carbon alkane aldehyde and a lower alkane  $\alpha$ -diketone and with furfuryl mercaptan. It has been found that any

desirable interactions which take place between and among the respective carbonyl and mercaptan compounds are relatively rapid so that it would be possible to either combine the compounds together before fixing or to fix one or more of these compounds separately from the other end and then combine the fixed materials. In this latter embodiment, the interactions between the separately fixed compounds would occur as the soluble product to which they are added is reconstituted immediately before consumption. As set forth in the Feldman et al. patent, the methyl mercaptan combines with the preceding carbonyl compounds to produce a desirable grinder gas aroma; however, unexpectedly in view of the teachings of Feldman et al., the present invention has found it desirable to add a relatively high level furfuryl mercaptan to add a desirable roasted note to the composition without causing any immediate undesirable interactions and without adding a foul smell, commonly described as rubber boot for furfuryl mercaptan. *Fenaroli's Handbook of Flavor Ingredients 2nd Edition* (Chemical Rubber Co. 1975) at Vol. 2, Pg. 209, notes the potential for furfuryl mercaptan to exhibit an unpleasant odor.

Desirably the unreacted and unfixed furfuryl mercaptan should not be permitted to remain in liquid state contact with the methyl mercaptan or carbonyl compounds for a prolonged period of time, especially if these compounds are present at a relatively concentrated level. Thus, when furfuryl mercaptan is combined with the other synthetic grinder gas components in a liquid state, conversion of the liquid mixture to a dry form should take place before the passage of several hours, preferably within two hours. It would, of course, be possible to fix furfuryl mercaptan in dry form, usually at levels below 1% by weight, away from the methyl mercaptan and carbonyl components.

It has been found that the preferred fixatives for use in this invention are water-soluble, hydrolyzed starch materials, such as low D.E. (dextrose equivalent) dextrans and corn syrup solids and that the aroma components can only be fixed at a relatively low level of below 10%, preferably below about 3% and typically between about 1% to 3% by weight of the fixative. Attempts to fix in dextrinlike materials at higher levels result in fixations which quickly dissipate a high percentage of aromatics. Efforts to employ fixatives consisting solely of materials such as gelatin or other materials which contain reactive groups, such as atmospheric coffee solids, or the solids extracted from a caramelized mixture of roasted wheat, bran and molasses (Postum®), have not proven as successful. It is believed that the reactive nature of the carbonyl and/or mercaptan compounds limits the choice of fixatives. Use of autoclave coffee solids, which consist essentially of high molecular weight compounds and low D.E. dextrans in combination with minor (less than 25%) amount of gums, such as gum arabic, may be employed.

## DETAILED DESCRIPTION OF THE INVENTION

The aroma composition of this invention is prepared by contacting a molar excess of carbonyl compounds with methyl mercaptan, the molar ratio being in the range of from 3:1 to 90:1 and preferably within the range of 20:1 to 50:1, and including in the composition an amount of furfuryl mercaptan at a weight ratio to methyl mercaptan of from 1:4 to 2:1. The aforementioned carbonyl compounds must include acetaldehyde,

preferably at a mole ratio to methyl mercaptan of from 2:1 to 50:1, a 4 or 5 carbon alkane aldehyde, preferably at a mole ratio to methyl mercaptan of from 0.02:1 to 3:1, and a lower alkane  $\alpha$ -diketone, preferably at a mole ratio to methyl mercaptan of from 0.2:1 to 5:1.

The preferred alkane aldehyde is isobutyraldehyde; however, isovaleraldehyde may be employed in place of or in addition to the isobutyraldehyde. The preferred alkane  $\alpha$ -diketones are 2,3-butanedione and 2,3-pentanedione. While mixtures of these diketones may be employed, it is preferred to employ a single diketone, particularly 2,3-butanedione. Desirably the aroma composition will also contain an amount of acetone, preferably at a mole ratio to methyl mercaptan of from 0.6:1 to 30:1. Other additives such as dimethyl sulfide may also be added to the synthetic grinder gas composition.

As mentioned previously, the synthetic grinder gas compounds are fixed in an inert fixative. As previously noted, all of these compounds may be fixed together or furfuryl mercaptan may be fixed away from the methyl mercaptan. The furfuryl mercaptan which has a boiling point of 155° C. and is insoluble in water may be separately fixed at a level below about 1% by weight, usually in combination with other higher-boiling enhancers. Typically the synthetic grinder gas fixation is accomplished by preparing a water solution of a dextrin fixative, such as a low D.E. (10 or less) hydrolyzed starch material exemplified by 10 D.E. Frodex (acid hydrolyzed corn syrup solids produced by American Maize Corp.) and 10 D.E. Mor-Rex (enzymatically hydrolyzed starch produced by CPC International Corp.), adding the grinder gas compounds at a level of from 1 to 3% by weight of the fixative to the water solution and then drying, such as by freeze-drying or spray drying. In commercial operation, generally it will be desirable to spray dry, preferably from a solution having a solids concentration of from 30 to 45% by weight. Spray drying should be effected at relatively low temperatures so as to minimize loss of volatiles. Inlet air temperature to the spray dryer should be from about 125° C. to 290° C.; air outlet temperature should be from 85° C. to 100° C.

In order to facilitate addition of the synthetic grinder gas compounds to the aqueous fixative solution, it is possible to dissolve the highly volatile compounds such as methyl mercaptan (B.P. 6° C.) in an edible organic solvent such as an alcohol which can to a great extent be removed during the drying step or in propylene glycol or triacetin which at the levels employed will not impart a detectable flavor to the end product. Likewise water-insoluble compounds such as furfuryl mercaptan can be first dissolved in an edible organic solvent prior to addition to the aqueous fixative solution.

Other known coffee enhancers such as the woody-flavored 2-nonenal and 2-nonenol compounds of U.S. Pat. No. 3,886,297 and the green earthy-flavored substituted pyrazine compounds of U.S. Pat. No. 3,767,425 may also be added to the soluble coffee or coffee-like products in order to increase their consumer appeal. It has been found, however, that these high-boiling compounds (boiling point above about 180° C.) should be handled apart from the low-boiling point compounds of the synthetic grinder gas formulation. These high-boiling compounds, optionally in combination with furfuryl mercaptan, will be added at low levels to a separate water solution of an edible fixative and then spray or freeze dried. The total amount of these enhancers to be

fixed should again preferably be less than 3% by weight of the fixative.

The fixed synthetic grinder gas compounds, together with other fixed enhancers, are combined with soluble foodstuff powders, soluble coffee and/or soluble coffee-like solids at the appropriate level in order to effect the desired aroma/flavor impact. Advantageously, the soluble foodstuff, coffee and coffee-like particles will be sized comparably to the fixed enhancers so that segregation of the particles will not occur in the final product. It would also be possible to co-agglomerate the various dry components. It has been found that the volatile compounds fixed at the low level specified in this invention are able to pass through a mild stream agglomeration step without significant loss of volatiles. The steam employed for agglomeration should preferably be saturated and have a temperature below about 135° C., typically about 120° C.

For purposes of this invention, the fixed furfuryl mercaptan is added to the soluble coffee-flavored foodstuff, coffee or coffee-like product at a level which will produce a furfuryl mercaptan concentration in the final product, as consumed, of from 20 to 80 parts per billion, preferably about 25 to 50 parts per billion. Since typically a soluble beverage powder is reconstituted to a beverage having a 1% by weight soluble solids level, the furfuryl mercaptan concentration in a beverage powder should be about 2 to 8 parts per million.

#### EXAMPLE 1

A 40% soluble solids aqueous solution of a 10 D.E. dextrin (Mor-Rex) was prepared to which a synthetic grinder gas formulation was added in order to produce a solution within the following compositional ranges. Methyl mercaptan was added to the dextrin solution by first dissolving methyl mercaptan in triacetin and then adding amounts of this triacetin solution containing the desired quantity of methyl mercaptan. The solution was spray dried in a co-current spray drier having an air inlet temperature of 130° C. and an air outlet temperature of 95° C.

Ingredient	Wt. %
Mor-Rex (10 D.E.)	94-98
Acetaldehyde	0.4-3.0
Acetone	0.1-2.0
Methyl Mercaptan	.04-0.2
Dimethyl Sulfide	.03-1.5
Isobutyraldehyde	.04-1.5
Isovaleraldehyde	.04-1.0
2,3-Butanedione	0.1-2.0

A second 40% dextrin solution was prepared to which was added furfuryl mercaptan, dissolved in triacetin, 2-nonenol, 2-isobutyl-3-methoxypyrazine and eugenol. The resulting solution having the following compositional ranges is spray dried under the same conditions recited above.

Ingredient	Wt. %
Mor-Rex (10 D.E.)	94-98
Furfuryl Mercaptan	.02-0.1
2-Nonenol	.06-0.4
2-Isobutyl-3-Methoxy pyrazine	.0004-.002
Eugenol	0.3-1.0



The two spray dried powders are blended together in equal amounts and agglomerated with spray dried coffee solids at a weight ratio of 5% fixed enhancers and 95% coffee. The agglomeration step is effected in a tower agglomerator fed with saturated steam at 121° C. and drying air having an inlet temperature of 143° C. and an outlet temperature of 93° C. The resulting coffee product is packaged in glass jars under an inert atmosphere. After several weeks of storage and upon the initial and subsequent openings of the jars, a pleasant coffee grinder gas aroma is apparent and upon dissolving the agglomerated powder in hot water, a coffee beverage having an improved taste and aroma over conventional soluble coffees is obtained.

#### EXAMPLE 2

The procedure of Example 1 was followed with the exception that the furfuryl mercaptan component was added to the dextrin solution containing the methyl mercaptan. In operation, separate solutions of methyl mercaptan dissolved in triacetin and furfuryl mercaptan dissolved in triacetin were added to the first dextrin solution and this solution also containing the other synthetic coffee grinder gas components was spray dried within two hours of being prepared to produce a fixed synthetic grinder gas material. The second dextrin solution containing the 2-nonenol, 2-isobutyl-3-methoxypyrazine and engenol components was spray dried as in Example 1 to produce a fixed synthetic coffee enhancer material. These two spray dried materials were agglomerated with soluble coffee solids as in Example 1 to produce a coffee product and coffee beverage which, upon being evaluated after several weeks storage, is comparable to the product and beverage of Example 1.

#### EXAMPLE 3

Fifty-six grams of a commercial vanilla instant pudding mix is combined with 3 grams of agglomerated soluble coffee powder from Example 2. The combined mix was added to a bowl containing 250 ml of cold milk and mixed until well blended and then allowed to set for several minutes. The pudding possesses a pleasant coffee flavor.

#### EXAMPLE 4

A coffee-flavored instant pudding mix is prepared by combining an unflavored instant pudding mix (51.5 grams), caramel color (1 gram), fixed synthetic coffee grinder gas material of Example 2 (0.1 grams) and fixed synthetic coffee enhancer material of Example 2 (0.06 grams). The combined mix is added to 250 ml of cold milk to produce a pudding as in Example 3. The pudding possess a pleasant coffee flavor.

#### EXAMPLE 5

A coffee-flavored beverage mix is prepared by combining a commercial non-dairy creamer powder (20 grams), powdered sugar (10 grams), caramel color (1 gram), fixed synthetic coffee enhancer material of Example 2 (0.48 grams), fixed synthetic coffee grinder gas material of Example 2 (0.18 grams), caffeine (0.1 grams), disodium pyrophosphate (0.2 grams) and tetrasodium phosphate (0.2 grams). This mixture was dissolved in 715 ml of hot water to produce a pleasant coffee-flavored hot beverage.

#### EXAMPLE 6

A powdered coffee-flavored, non-dairy creamer is prepared by combined 20.3 grams of a commercial non-dairy creamer powder, 20.3 grams of sugar, 0.3 grams of the fixed synthetic coffee grinder gas material of Example 2 and 0.25 grams of the fixed synthetic coffee enhancer material of Example 2. The mix is added to one liter of hot coffee to produce a lightened coffee beverage having an excellent coffee flavor.

#### EXAMPLE 7

A coffee-flavored grain beverage mixed is prepared by combining 24 grams of instant Postum®, a dried extract of roasted bran, wheat, and molasses, 0.4 grams of the fixed synthetic coffee grinder gas material of Example 2 and 0.3 grams of the fixed synthetic coffee enhancer material of Example 2. This mix is added to one liter of hot water to produce a hot beverage having an excellent coffee flavor.

What is claimed:

1. A method for preparing a soluble, enhanced coffee-flavored foodstuff, coffee and/or coffee-like product comprising the steps of:
  - (a) adding methyl mercaptan and a molar excess of carbonyl compounds, including for each mole of methyl mercaptan 2 to 50 moles of acetaldehyde, 0.02 to 3 moles of a 4 to 5 carbon alkane aldehyde and 0.2 to 5 moles of a lower alkane  $\alpha$ -diketone selected from the group consisting of 2,3-butanedione, 2,3-pentanedione and mixtures thereof, to an aqueous solution of a non-reactive fixative, said materials being added in a total amount less than 10% by weight of the fixative,
  - (b) drying the solution from step(a),
  - (c) adding furfuryl mercaptan to an aqueous solution of a non-reactive fixative at a level below about 1% by weight of the fixative,
  - (d) drying the solution of step (c),
  - (e) combining the dried materials from steps (b) and (d) with soluble particles of a powdered foodstuff, coffee and/or coffee-like material, such that furfuryl mercaptan is present in an amount of from 2 to 8 parts per million by weight of the combined material and also present in an amount of from 1:4 to 2:1 by weight of methyl mercaptan.
2. The method of claim 1 wherein the weight of materials added in step (a) in less than 3% by weight of the fixative.
3. The method of claim 2 wherein the drying in steps (b) and (d) is effected by low-temperature spray drying.
4. The method of claims 2 or 3 wherein the dry combination of step (e) is agglomerated by means of saturated steam having a temperature below 135° C.
5. The method of claim 3 wherein one or more coffee enhancers having a boiling point in excess of 180° C. are added to the solution of step (c) at a level such that the total amount of enhancers fixed is less than 3% by weight of the fixative.
6. The method of claim 5 wherein 2-nonenol or 2-nonenal is added to the solution of step (c).
7. The method of claim 1 wherein the fixative of steps (a) and (c) is a hydrolyzed starch material having a dextrose equivalent of 10 or less.
8. A method for preparing a soluble, enhanced coffee-flavored foodstuff, coffee and/or coffee-like product comprising the steps of:



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(a) adding methyl mercaptan, a molar excess of carbonyl compounds, including for each mole of methyl mercaptan 2 to 50 moles of acetaldehyde, 0.02 to 3 moles of a 4 to 5 carbon alkane aldehyde and 0.2 to 5 moles of a lower alkane  $\alpha$ -diketone selected from the group consisting of 2,3-butanedione, 2,3-pentanedione and mixtures thereof, and furfural mercaptan in an amount of from 1:4 to 2:1 by weight of methyl mercaptan to an aqueous solution of a non-reactive fixative said materials being added in a total amount less than 10% by weight of the fixative.

(b) drying the solution from step (a),

(c) combining the said material from step (b) with soluble particles of a powdered foodstuff, a coffee and/or a coffee-like material such that furfuryl mercaptan is present in an amount of from 2 to 8 parts per million by weight of the combined material.

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9. The method of claim 8 wherein the weight of materials added to step (a) is less than 3% by weight of the fixative.

10. The method of claims 8 or 9 wherein one or more coffee enhancers having a boiling point in excess of 180° C. are added to an aqueous solution of a non-reactive fixative at a level such that the total amount of enhancer fixed is less than 3% by weight of the fixation, said solution is dried and the dried material combined with the dry powdered foodstuff, soluble coffee or coffee-like material of step (c).

11. The method of claim 10 wherein 2-nonenol or 2-nonenal is added as a coffee enhancer having a boiling point about 180° C.

12. A method of claim 8 wherein the fixation is a hydrolyzed starch material having a dextrose equivalent of 10 or less.

13. The method of claim 8 wherein the drying is effected by low-temperature spray drying.

14. The method of claim 10 wherein the combined materials are agglomerated by means of saturated steam having a temperature below 135° C.

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